

English Translation of JP 63-8408

* NOTICES *

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 2. The word which can not be translated is expressed by Japanese character.
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[Claims for the Patent]

[claim 1]

In ethylene, carbon number 3 - ten α - olefin and ethylene copolymer gum made up of polyene, polyene is, five - ethylidene -2 - ノルボルネン (ENB) and five - vinyl -2 - ノルボルネン 50/50 - 95/5 ethylene / α - olefin (mole ratio) (b) (a) (VNB), and the component ratio ENB/VNB (mole ratio) is iodine number 2 - 50, limiting viscosity $[\eta]$ 0.7 measured in 135 degrees Celsius decalin (d) - 6.0dl/g, ethylene / α - olefin polyene random copolymer gum including Q value (weight average molecular weight / number average molecular weight) appears very much than 6 (e), and there being 1/1 - 45/1 (c).

[claim 2]

ENB/VNB (mole ratio) is 20/1 - copolymer rubber as claimed in claims Clause 1 in 45/1 ranges.

[claim 3]

Rate $g^*([\eta] / [\eta]_1)$ of $[\eta]$ for limiting viscosity $[\eta]_1$ of normal chain ethylene propylene random copolymer of 70 mol % is copolymer gum as claimed in claims Clause 1 in field of 0.2 - 0.94 ethylene content to show the same weight average molecular weight (by light scattering method).

[Detailed Description of the Invention]

(a field of industrial application)

The present invention is related to ethylene, carbon number 3 - random 4 yuan copolymer gum comprising ten α - olefin, five - ethylidene -2 - ノルボルネン (ENB) and five - vinyl -2 - ノルボルネン (VNB).

(prior art)

As a representative person of terpolymer rubber, ethylene, .5- propylene ethylidene -2 - ノルボルネン (ENB) inter-polymerization rubber and ethylene propylene

dicyclopentadiene copolymerization gum are known.

As for the inter-polymerization rubber of the former, vulcanization speed is big, and extruding characteristics are bad, and there is shortcoming that it is difficult to mold as a molded article having the pushing out skin which is particularly beautiful by high speed escalope extrusion although strength of vulcanizate has an advantage to be big.

In addition, inter-polymerization rubber of the latter has the advantage that extruding characteristics can be superior to, but vulcanization velocity is late, again, a vulcanization hardness haze, it is inferior.

That polyene ingredients more than two kinds are used is suggested conventionally for the purpose of improving many characteristic properties of such an inter-polymerization rubber (cf. 44 Japanese Patent Laid-Open No. - 7713, 47-23914, 49-62582, 49-62583 bulletin).

(the problems that should be settled)

However, a configuration holdout is not yet enough without can take pushing out processing characteristics, vulcanization speed and balance of vulcanization hardness in inter-polymerization rubber of the prior art enough.

Thus, a problem of technology of the present invention is to succeed in getting improvement a configuration holdout as well as many characteristic such as pushing out processing characteristics, vulcanization speed and vulcanization hardness conspicuously.

(means to solve problems)

As for the 4 yuan copolymer rubber of the present invention, it is from ethylene, carbon number 3 - ten α - olefin, five - ethylidene - 2 - ノルボルネン (ENB) and five - vinyl - 2 - ノルボルネン (VNB) (a), ethylene / α - olefin (mole ratio), 50/50 - 95/5, (b), ENB/VNB (mole ratio), 1/1 - 45/1, (c), iodine number 2 - 50, limiting viscosity $[\eta]$ 0.7 measured in 135 degrees Celsius decalin (d) - 6.0dl/g, Q value (weight average molecular weight / number average molecular weight) appears very much than 6 (e), and there being, in constitution, it is characterized.

(operation)

In inter-polymerization rubber of the present invention, mole ratio (characteristic (a)) with ethylene and α - olefin affects physical property of flexibility of rubber and vulcanized rubber. Ethylene content will be that is to say inferior to the range in flexibility when it is high, in addition, physical properties of vulcanized rubber will be inferior to the range when it is low.

In addition, the component ratio (characteristic (b)) of ENB/VNB influences a shape

holdout, pushing out skin and physical properties of vulcanized rubber. It is that is to say when there is too few component ratio of VNB when unsatisfactory in a shape holdout and pushing out skin, when there is too much again, physical property of vulcanized rubber becomes bad.

Iodine number (characteristic (c)) is a factor showing content of the polyene ingredient.

It is factor expressing molecular size of inter-polymerization rubber, and limiting viscosity $[\eta]$ (above characteristic (d) measured in 135 degrees Celsius, decalin) influences roll workability, gum hardness and extrusion characteristics. This limiting viscosity $[\eta]$ comes to have difficulty with abrasive roll processing with under 0.7dl/g, and it is when, in addition, it is unsatisfactory in rubber hardness, when it is very much than 6.0dl/g, roll retention characteristics and extrusion characteristics turn worse.

In addition, in the present invention, a shape holdout improves by a thing (characteristic (e) in the constitution) Q value conspicuously very much than 6.

As it is that is to say clear from an example to be described below, when Q value is inter-polymerization rubber very much than 6, and θ is equal to or less than, and about 15 sauce angle is often found, there is little deformation, and what a configuration holdout can be superior to is recognized by being lower than ten $^\circ$.

If it goes, a reason of shape retention improving in the present invention is not yet clear, but people of present invention suppose like next.

Because copolymer rubber of the present invention is that is to say soluble in boiling hexane, is afraid that high, crosslinking substance. However, it will be understood that weight average molecular weight Mw (by light scattering method) shows a big value for limiting viscosity, thing by Q value showing a big value. Thus, by the end of a copolymer rubber molecule of the present invention, it is conceivable that bridging structure is not a little formed, it seems whether a configuration holdout does not improve due to this cross-link configuration conspicuously.

(operation/working-effect)

Copolymer rubber of the present invention be superior in a shape holdout conspicuously, and a first surface of an extrusion is flatness, and flowability is good again, and sponge rubber and compression set when it was done have characteristic to be small.

It is preferable, and rubber of the present invention to take is used for use with a weather striptease, ドアークラスランチャンネル, various hoses, a sponge for various seals, insulation sponge tube, electric wire coating material, various

patternized stage molded articles and roofing sheet.

(preferred embodiment of invention)

Rubber composition

Inter-polymerization rubber of the present invention is ethylene, carbon number 3 - random copolymer of ten α - olefin, ENB and five - vinyl -2 - ノルボルネン (VNB).

For carbon number 3 - ten α - olefin, propylene, one - butene, one - pentene, one - hexene, four - carbonyl -1 - pentene, one - octene, one - decene, blending olefin of higher than two kinds of these option can be exemplified. Particularly preferred α - olefin is propylene and one - butene.

As for the component ratio with ethylene and α - olefin, there are ethylene / α - olefin = 50/50 - 95/5 in field of 55/45 - 85/15 with a mol standard preferably. This component ratio can be found from the measurement of absorbance by infrared spectrophotometer or the strength measurement with a C^{13} NMR spectrum meter.

ENB/VNB = 1/1 - 45/1 are preferable, and 2/1 - 40/1 are more desirable, and there is the component ratio with ENB and VNB in field of 20/1 - 40/1 with a mol standard.

The ENB/VNB component ratio in copolymer rubber can demand by analyzing content with ENB and VNB of unreacting of the whole strength measurement with a C^{13} NMR spectrum meter or polymerization fluid in gas chromatography.

Limiting viscosity $[\eta]$

There is limiting viscosity $[\eta]$ measured in 135 degrees Celsius of copolymer rubber of the present invention, decalin in 0.7 - 6.0 dl/g, 0.8 in particular - field of 4.0 dl/g.

This limiting viscosity is a factor expressing molecular size of copolymer rubber.

Iodine number

There is iodine number of copolymer rubber of the present invention in 2 - 50, 3 in particular - 45 ranges.

This iodine number is a factor expressing content of the polyene ingredient of rubber.

Q value

In inter-polymerization rubber of the present invention, Q value by GPC (gel permeation chromatography) (weight average molecular weight / number average molecular weight) is a size than 6, but a shape holdout improves particularly conspicuously, besides, there is a superior thing in field of less than or equal to 20 in strength and balance of conversion characteristics very much than 7.5.

In addition, the measurement of Q value follows written by Takeuchi, 'gel permeation chromatography' of published by Matuzen, and it is resembled like next, and it is

performed.

(1) Using molecular weight known normal polystyrene () monodisperse polystyrene made by Orient soda (), molecular weight M and the GPC (Gel Permeation Chromatograph) count are measured, correlation diagram calibration curve of molecular weight M and EV (Elution Volume) is made. The density of this time assumes 0.02wt %.

(2) GPC chromatograph of sample is taken by the GPC measurement, it is number average molecular weight of polystyrene conversion by the (1)

Weight average molecular weight is calculated, Q value (M_w/M_n) is found. Sample preparation condition of the case and a GPC measurement condition are as follows.

A sample preparation

Fractionation does (a) sample in Erlenmeyer flask with *o*-dichlorobenzene solvent to become 0.04wt %.

(b) 0.1wt % adds age resistor 2,6-di-tert-butyl-p-cresol in the Erlenmeyer flask which sample is in as against polymer solution.

(c) Erlenmeyer flask is warmed to 140 degrees Celsius, it is stirred for about 30 minutes, it makes dissolve.

(d) In 135 degrees Celsius – 140 degrees Celsius, it is filtered in one μ Millipore filter afterwards.

(e) The filtrate is bet on GPC.

A GPC measurement condition

It was carried out under conditions of next.

(a) 200 models made in device Waters company

(b) column Orient soda (a product made in)

A S- type (a Mix type)

(c) Sample quantity 2ml

(d) temperature 135 degrees Celsius

(e) speed of flow 1ml/min

Total number of theoretical plate $2 \times 10^4 - 4 \times 10^4$ of a (f) column

Copolymer rubber of the present invention shows big weight average molecular weight $\langle M \rangle_w$ (by light scattering method) for limiting viscosity (measured value by acetone) by showing to that big Q value. When when it is shown to that this by another expression method, $[\eta]$, weight average molecular weight at that time is done with $\langle M \rangle_w$ in limiting viscosity of inter-polymerization gum of the present invention, molecular weight of, $\langle M \rangle_w$ is had, Q value (weight average molecular weight / number average molecular weight by GPC), 2.5 normal chain ethylene propylene copolymer (when

it is assumed limiting viscosity $[\eta]$ of ethylene content 70 mol %), and it is defined as calculation $[\eta] / [\eta]_0 = g \eta^*$ by $= 7.2 \times 10^{-4} \langle [\eta] / M \rangle W_0$. 67s there is in $g \eta^* 0.2 - 0.94$, 0.4 in particular - 0.93 ranges.)

In this way, as for $g \eta^*$ more considerably than 1 showing a small value, it is afraid that existence of cross-link configuration other than short-chain branching due to the α - olefin which is copolymerization constituent with ethylene.

As for the inter-polymerization rubber of the present invention, is that is to say afraid that high, crosslinking substance in what is soluble in boiling hexane, but cross-link configuration is not a little formed, is estimated that a configuration holdout improves as for the copolymerization gum of the present invention conspicuously by this.

Compound agent

To copolymer rubber of the present invention, lower than part by weight, tenderizer 250 can be blended in with lower than part by weight, cure agent 0.1 - 20 part by weight and vulcanization accelerator 0.1 - quantity of 20 part by weight with filler 300 per compounding for rubber of it in itself public intellect, 100, for example, copolymer gum part by weight.

For filler, inorganic filler such as carbon black, white carbon (Kay acid compound), calcium carbonate, purified talc, clay, Organic filler such as high styrene resin, coumarone and indene resin, a phenolic plastic, lignin, property modification melamine resin, petroleum resin can be given. Of these, it is preferable, and inorganic filler in particular is used.

Tenderizer pro-oil such as processing oil, lubricating oil, paraffin, adepsine oil, oil asphalt, paraffin jelly for tenderizer, Coal tar system tenderizer such as coal tar, coal tar pitch, Fatty oil system tenderizer such as castor oil, linseed oil, a rapeseed oil, coconut oil, Tall oil, Sub, Low such as dense low, カルナウバロウ, a refined wool fat, 12-hydroxyoleic acid, palmitin acid, barium stearate, calcium stearate, fatty acid such as zinc laurate and fatty acid salt, Synthetic polymeric substances such as petroleum resin, を can be given.

For cure agent, metal compound such as peroxide, sulfur, sulfur monochloride, sulfur dichloride, morpholine disulfide, alkylphenol disulfide, tetramethylthiuram disulfide, sulfur compound such as dimethyldithiocarbamic acid Se, magnesium oxide, zinc oxide, red lead can be given. Above all, sulfur or peroxide is preferable. For vulcanization accelerator, thiazole system such as N- cyclohexyl -2 - benzothiazole - スルフエンアミド, N- Oki ti diethylene -2 - benzothiazole - スルフエンアミド, N, N - diisopropyl -2 - ベンゾチアゾールスルフエンアミド, two - mercaptobenzothiazole,

two - (2,4- dinitrophenyl) mercaptobenzothiazole, two - (2,6- diethyl -4 - モルホリノチオ) benzothiazole, ベンゾチアジル - disulfide, Guanidine system such as diphenylguanidine, triphenyl guanidine, di- ortho - tolyl guanidine, ortho - トリルバイグアナイド, diphenylguanidine phthalate, Acetaldehyde - aniline reactant, Butylaldehyde - aniline condensate, hexamethylene tetramine, aldehyde amine such as acetaldehyde ammonia or aldehyde - ammonia system, Imidazoline type such as two - mercapto imidazoline, チオユリア system such as チオカルバニリド, diethylthio lily horse mackerel butylthio urea, trimethylthio urea, di- ortho - tolylthio urea, Thiuram system such as tetramethylthiuram monosulphide, tetramethylthiuram disulfide, tetramethylthiuram disulfide, tetrabutyl thiuram disulfide, dipentamethylene thiuram tetrasulphido, Dithioic acid salt system such as dimethyldithiocarbamic acid zinc, diethylthio carbamic acid zinc, di-n- butyl dithiocarbamate zinc, ethylphenyl dithiocarbamate zinc, butylphenyl dithiocarbamate zinc, sodium dimethyldithiocarbamate, dimethyldithiocarbamic acid Se, diethyldithiocarbamate Te, Xanthate system such as dizinc butylxanthate, などを can be given.

In addition, others can use activator, dispersing agent, plasticizing material, tackifier, pigmenting drug, blister agent, foaming auxiliary, lubricant, age resistor, others additive together if necessary.

By way of example only, as plasticizing material, sodium bicarbonate, ammonium carbonate, N, N ' - dinitrosopentamethylenetetramine, azo carbonamido, azobisisobutyronitrile, benzene sulfonyl hydrazide, toluenesulfonyl hydrazide, calcium azide, para toluenesulphonylazide can use salicylic acid, phthalic acid, urea as tackifier such as phthalic acid ester, adipic acid ester, sebacic acid ester, phosphoric acid system for effervescence auxiliary for inorganic organic pigment to invite blister agent for colorant such as coumarone and indene resin, a terpene phenolic plastic, xylene formalin resin.

Vulcanization

Inter-polymerization rubber of the present invention can do vulcanization with normal ethylene propylene polyene inter-polymerization rubber similarly.

Vulcanization can be done in both sulfur vulcanization and peroxide vulcanizing system.

For this case, as peroxide, dicumyl peroxide, 3,3,5-1,1 ' - di- (t- butyl peroxy) - trimethylcyclohexane, di- (t- butyl peroxy) diisopropyl benzene, 2,5- dimethyl - 2,5- di- (t- butyl peroxy) hexane are exemplified. In addition, independent, or, as vulcanization auxiliary of the case, oxime chemical agent such as sulfur, sulfur

compound such as dipentamethylene thiuram tetrasulphido, ethylenedimethacrylate, divinylbenzene, diallylphthalate, meta phenylene bismaleimide, the polyfunctional monomer which seem to be toluylene bismaleimide, p-quinone dioxime, p,p'-dibenzoyl quinone oxime is mixed, and it can be used.

Vulcanization conditions are different by a kind of cure agent, but preferably preferably, normal 100 - 250 degrees Celsius, line Uno is preferable in 120 - temperature of 200 degrees Celsius for 20 - 40 minutes for 10 - 60 minutes. When peroxide vulcanization in particular is done, vulcanizing time had better assume around 4 times of a half value period of peroxide.

Production of copolymer rubber

For example, random copolymerization should do α -olefin of existence bottom of catalyst formed by organoaluminum compound shown in vanadium compound expressed in soluble vanadium compound, for example, -type VO (OR) nX_3-n (but, R, hydrocarbon group, X, Halogen, $0 \leq n \leq 3$) or VX₄ (a) and (b) R' $mAlX'$ $3-m$ (but, R', hydrocarbon group, X', Halogen, $0 < m < 3$), ethylene, carbon number 3 - 10, ENB and VNB in wish composition and the rate that it is among hydrocarbon medium to produce inter-polymerization rubber of the present invention.

As an operative example of vanadium compound shown to in the general formula, VO (OCH₃) Cl₂, VO (OCH₃) 2Cl, VO (OCH₃) 3, VO (OC₂H₅) Cl₂, VO (OC₂H₅) 1.5Cl 1.5, VO (OC₂H₅) 2Cl, VO (OC₂H₅) 3, VO (OC₂H₅) 1.5Br 1.5, VO (OC₃H₇) Cl₂, VO (OC₃H₇) 1.5Cl 1.5, VO (OC₃H₇) 2Cl, VO (OC₃H₇) 3, VO (On - C₄H₉) Cl₂, VO (On - C₄H₉) 2Cl, VO (OisoC₄H₉) 2Cl, VO (OsecC₄H₉) 3, VO (OC₅H₁₁) 1.5Cl 1.5, VOCl₃, VCl₄ or mixture of these can be exemplified. In these, it is particularly preferable to use VO (OC₂H₅) Cl₂, VOCl₃.

If, for organoaluminum compound shown to in the expression, m 0.5 clear up $\leq m \leq 2.5$, a thing of one $\leq m \leq 2$ is desirable. For example, (CH₃), for such an organoaluminum compound, 1.5AlCl 1.5 can exemplify AlCl₂ or these mixtures 2AlCl AlCl₂ 1.5AlCl 1.5 2AlCl AlCl₂ 1.5AlCl 1.5 2AlCl (C₆H₁₃) (C₆H₁₃) (C₆H₁₃) (C₃H₇) (C₃H₇) (C₃H₇) (C₃H₇) (C₂H₅) (C₂H₅) (C₂H₅) (CH₃) (CH₃).

2 - 50, 5 in particular - 30 field is desirable for a use ratio of organoaluminum compound and a パナジウム compound as Al/V (the atom ratio).

Inter-polymerization can be done in hydrocarbon medium. By way of example only, independent, or the aromatic hydrocarbon which seems to be hexane, heptane, octane, aliphatic hydrocarbon such as kerosene, the alicycle family hydrocarbon which seem to be cyclohexane, benzene, toluene, xylene is mixed, and it can be used as solvent. Or a surplus of α -olefin is used, and it can be assumed reaction media.

Preferably, as for the inter-polymerization, it is desirable for 0.1 - density of

2 millimeters mol / L vanadium compound 0.01 - 5 millimeters mol / L among reaction media that it is. A supply ratio of α - olefin is different from ethylene by polymerization condition, but it is 20/80 - around 80/20, and, as for the feed ratio of ENB and VNB, is usually done 1/1 - 60/1 with 2/1 - field of around 50/1 in mole ratio in normal mole ratio particularly again. Preferably, in general terms, preferably, as for the polymerization temperature, as for 20 - 80 degrees Celsius, the polymerization pressure force, it is held 0 - 50kg/cm² to 0 - 20kg/cm² 0 - 100 degrees Celsius to the public. It can make there be molecular weight modifier such as hydrogen for molecular weight regulation of inter-polymerization rubber appropriately.

(an example)

Example 1

Polymerization vessel made by stainless of 15L comprising a churn feather was used, and 4 yuan copolymerization reaction of .5- five ethylene propylene ethylidene -2 - ノルボルネン・ - vinyl -2 - ノルボルネン was performed continually.

In other words hexane is supplied at the rate of 5L as polymerization solvent continually every hour from the polymerization vessel upper part.

On the other hand, polymerization fluid is pulled out serially so that polymerization liquid in polymerization vessel always becomes 5L from polymerization vessel lower part.

VOC13, Al (C₂H₅)₂Cl and Al (C₂H₅)_{1.5}Cl_{1.5} were used as a catalytic substance.

As for VOC13, aluminium atom density of the whole polymerization vessel that is to say supplied Al (C₂H₅)₂Cl and Al (C₂H₅)_{1.5}Cl_{1.5} by the end of polymerization vessel serially again so that the vanadium atom density in polymerization vessel became 0.55mmol/ L so that it was with each 1.98mmol/ L, 1.32mmol/ L.

The ethylene of principal monomer supplied 170L /hr and the propylene at the rate of 375L /hr consecutively. In addition, five-ethylidene -2 - ノルボルネン and five - vinyl -2 - ノルボルネン supplied consecutively so that the density in polymerization vessel became each 6.7g/ L, 0.35g/ L.

In addition, hydrogen is used as molecular weight modifier, this was supplied so that the hydrogen density of a polymerization vessel gas phase became 3.1 mol %.

The copolymerization reaction performed in temperature of 40 degrees Celsius by circulating cooling water to a polymerization vessel outer jacket.

When copolymerization reaction is performed in a condition expressed in the above, .5- five ethylene propylene ethylidene -2 - ノルボルネン・ - vinyl -2 - ノルボルネン copolymer is provided in uniform solution state. A little methanol is

added by the end of polymerization liquid pulled out from polymerization vessel lower part, and polymerization reaction is stopped, after having divided polymer from solvent in steel stripping treatment, vacuum drying was done at 80 degrees Celsius in twenty-four hours.

5- five ethylene propylene ethylidene -2 - ノルボルネン・ - vinyl -2 - ノルボルネン copolymer was provided at the rate of 265g an hour by the above-mentioned operation.

The ethylene content of copolymer was 74 mol %, limiting viscosity $[\eta]$ 2.65dl/g, iodine value 21.1, five /5- - ethylidene -2 - ノルボルネン vinyl -2 - ノルボルネンモル ratios 23.1/1, Q value 8.6, $g \eta$ *0.88.

By the following prescription, 8 inches open abrasive roll is used, and provided copolymer rubber is kneaded at roll skin temperature 60 degrees Celsius for 25 minutes, compound was prepared.

Prescription

Ethylene / 100 α - olefin copolymer rubber part by weight

Five zinc oxide "

One stearic acid "

45 FEF carbon black "

30 paraffin series process oil part by weight

One tetramethylthiuram monosulphide (TMTM) "

One sulfur "

About provided compound, Mooney viscosity, optimum vulcanizing time, a sauce angle, surface roughness of an extrusion and rate of shear were measured. Each measuring method is as follows.

Mooney viscosity, It was measured at temperature of 125 degrees Celsius in accordance with JISK6300.

Optimum cure length of time T90; Osh rating cap liner rheometer (a product made in Monsanto Co.) was used, and it was measured as length of time before reaching 90% of effective torque in temperature of 160 degrees Celsius.

A sauce angle, Testing equipment of a sauce angle is shown to FIG. 1.

In FIG. 1, sample bar (25mm wide, 90mm long, single sheet thickness 2mm) 2 is that is to say put on sample bar mount 1 of steel of single sheet thickness 5mm, screw 3, 3 are used, and sample bar 2 is fixed with presser bar 4.

After this was held by the end of air oven of 50 degrees Celsius for 10 minutes, sauce angle θ ,

It was calculated by $\theta = \arctan (h/40)$.

In addition, a sample bar used mold tool of inside dimension method 130*110*2mm, and it was compressed in heat press of 50 degrees Celsius for 10 minutes, and it was made. Polyester film was used for prevention of adhesion with mold tool.

This sauce angle shows a shape holdout, a shape holdout is good so that this value is small.

Surface roughness, Surface roughness of an extrusion uses die loss diameter 1.5mm ϕ , die of L/D10 in capillary tube エクストルーション・レオメータ, surface of strand pushed in 120 degrees Celsius, rate of shear 395sec⁻¹ is measured in a surface roughness plan (surf com 200R type, a product made in Tokyo Seimitsu Corporation), it was shown in ten points of mean coarseness Rz.

Rate of shear, It showed in rate of shear (sec⁻¹) when it was pushed with shear stress 2.4×10^6 (dyne/cm²) at 120 degrees Celsius in capillary tube エクストルーション・レオメータ.

This rate of shear shows press, injection and flow properties in mold tool in transfer molding.

Vulcanized rubber physical properties, The thing which press vulcanization made the compound for 160 degrees Celsius, 30 minutes was measured in accordance with JISK6301.

In addition, the compression set performed under conditions of 25% compression for 100 degrees Celsius, 22 hours.

In above-mentioned example 1, various measurement results such as properties of copolymer rubber are shown to table 1 and table 2 respectively.

Example 2-9, comparative example 1-7

In example 1, copolymer of a different property was got by changing various kinds of polymerization condition.

Provided copolymer was evaluated same as example 1. Copolymer properties are shown to table 1.

Example 10

OOC type Vamba Lee mixer (a product made in Kobe Steel) was used, and five zinc oxide part by weight, two stearic acid overlapped portions, 120 SRF carbon black part by weight, 65 paraffin series process oil part by weight were kneaded in 100 copolymer part by weight of example 1 in about 150 degrees Celsius, six minutes. A provided thing to knead is cooled to about 70 degrees Celsius, in 14 inches open abrasive roll of about 60 degrees Celsius abrasive roll skin temperature, cure agent, vulcanization accelerator, blister agent are kneaded in about 10 minutes.

effervescence business composition of follows composition was got.

This composition is led in die and hot wind vulcanization cisterna (a product made in micro-electronic company) set to extrusion, 220 degrees Celsius to continue later in extrusion rate for 1.5m/ at head temperature 80 degrees Celsius, barrel front zone temperature 70 degrees Celsius, rear temperature 60 degrees Celsius in screw diameter 50mm ϕ , extruder (a product made in Tanabe plastic company) of L/D12 serially, it made complete vulcanization and effervescence in detention time six minutes, and sponge rubber was got.

In addition, a cross section end elevation of a provided rubber sponge was shown to FIG. 2. If, as for fleshy about 2mm, the internal diameter, there is not a form break, 16mm, breadth of a monotonous department are 20mm.

This rubber sponge is used, a method prescribed in swelling rubber physics testing method of association of Nippon Rubber standard norm was followed, and it was about to be watched, and specific gravity was measured. In addition, this rubber sponge is used, compression set, shape retention, surface roughness were measured.

Compression set compresses 50% substantial amount between AB of FIG. 2, after having held by the end of an oven of 70 degrees Celsius for 22 hours, it was demanded according to measuring method of JISK6301.

Shape retention measures space D of EF of FIG. 2 and space H of a CD (H/D), it was demanded as ± 100 (%).

When it was applied to example 1 along a longitudinal borderline including A point, surface roughness used the same surface roughness plan, and it was demanded with ten points of mean coarseness.

Comparative example 8

It is the same as example 7 except that copolymer used with comparative example 2 is used.